Contaminants of Emerging Concern During *De Facto* Water Reuse

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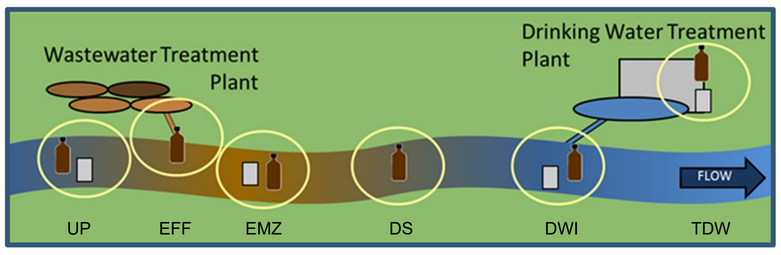
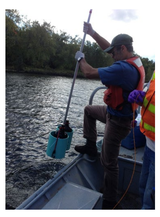
Abstract

The drinking water and wastewater cycles are integrally linked. Chemicals that are present in household wastewater may be sufficiently mobile and recalcitrant to pass through on-site or municipal wastewater treatment and survive natural environmental removal processes. Such persistent compounds have the potential to reach surface and ground waters that may be a source of drinking water. The US Environmental Protection Agency and US Geological Survey are collaborating to examine the sources, fates, and potential effects of contaminants of emerging concern (CECs) during *de facto* water reuse which occurs when treated wastewater is discharged to a source of drinking water. The project sampling design follows a surface flow path, with the collection of grab water samples from upstream of a wastewater treatment plant outfall and downstream to a drinking water treatment plant intake and through the plant to a finished water sample. The study uses an integrated approach that includes a comprehensive analysis of over 200 specific chemicals (e.g. pharmaceuticals, per- and polyfluoroalkyl substances); high resolution mass spectrometry to identify non-targeted (unknown) chemicals; *in vitro* bioassays (e.g. estrogenicity, androgenicity); rapid whole organism screens to assess cumulative bioactivity; and *in vivo* tests to address specific exposure and response endpoints. A rigorous quality assurance/quality control protocol was consistently applied from field to laboratory to ensure comparability of results between different techniques. This consistent, integrated approach combines the strength of each technique and builds upon the traditional CEC research approach by including environmental and toxicity endpoint assessments to more fully explore the potential effects to human health and the environment from chemical exposures. This presentation focuses on the results of the organic and inorganic chemical analyses.

Methodology





Three rounds of sampling (**October 2014, April 2015** and **August 2015**) were conducted in one watershed. In each round, grab samples were collected at six sampling points: 1) **Upstream (UP)** of a wastewater treatment plant; 2) **Wastewater Effluent (EFF)** where the pipe from the wastewater treatment plant enters the river; 3) the **Effluent Mixing Zone (EMZ)**, where the effluent is well mixed with the river body; 4) a **Downstream (DS)** sampling point; 5) a **Drinking Water Intake (DWI)** where water enters a drinking water treatment plant; and 6) **Treated Drinking Water (TDW)** before it enters the clear well of the treatment plant. Grab samples were collected in the UP, EMZ and DS locations using two 4-L silanized amber glass bottles dipped 0.5 m below the surface using the apparatus pictured above; in the EFF, a clean 4-L silanized amber bottle was placed in the wastewater pipe to fill. At these sampling points, the collected water was decanted into sample bottles pre-spiked with any required preservative or dechlorination agent. The drinking water treatment plant had plumbed sampling taps, so both the DWI and TDW samples were collected directly into the sampling bottles. Polar organic compound integrative samplers (POCIS) were also deployed at the UP, EMZ, DWI and TDW locations, but that data is not part of this presentation.

For the organic chemicals, samples were collected in triplicate with one designated the **primary,** one as a **duplicate**, and the third as a **laboratory fortified matrix** (LFM, aka matrix spike). Each sampling round was accompanied by three field blank samples.

Samples were analyzed for pharmaceuticals, per- and polyfluoroalkyl substances, (PFAS), hormones, sucralose, 1,4-dioxane, disinfection by products, and inorganic constituents by a suite of 11 different analytical methods, encompassing a total of 236 individual analytes. Inorganics were not analyzed in the DS, DWI, or TDW samples of Round 1, and PFAS were not analyzed in any of the Round 2 samples.

Results and Discussion

QA/QC Data Quality Objectives and Censoring

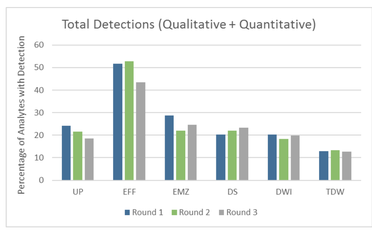
Performance Measure	Action		Number of Affected Measurements Across 236 Organic and Inorganic Analytes					
			UP	EFF	EMZ	DS	DWI	TDW
Matrix spike associated with sample > 150% recovery	Qualitative detection	Overall	1	19	2	3	3	0
		Round 1	1	7	1	1	3	0
		Round 2	0	5	0	1	0	0
		Round 3	0	7	1	1	0	0
Concentration less than LCMRL or RL	Qualitative detection	Overall	37	54	46	43	35	14
		Round 1	12	23	15	14	14	9
		Round 2	16	23	20	16	13	2
		Round 3	9	8	11	13	8	3
Sample concentration does not exceed 3 × field and/or laboratory blank concentration	Detection censored	Overall	13	1	11	8	14	10
		Round 1	5	0	4	3	5	4
		Round 2	4	1	4	2	4	3
		Round 3	4	0	3	3	5	3

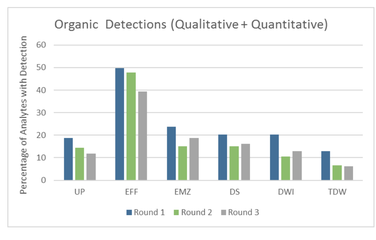
For a detection to be considered a quantitative detection, three data quality objectives had to be met: 1) it had to be above the Lowest Concentration Minimum Reporting Level (LCMRL) or reporting level (RL) for the analyte, 2) the associated LFM had to have a recovery less than 150%, indicating minimum matrix enhancement and 3) the concentration had to be greater than 3 times the associated laboratory and/or field blanks. Failing to meet either of the first two criteria resulted in the detection being deemed qualitative. If the sample failed the third criteria, it was censored and treated as a non-detect.

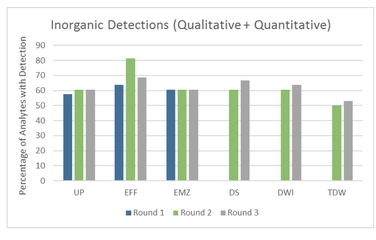
The above table summarizes the QA/QC actions taken across the 236 inorganic and organic chemicals. In general the Effluent and Effluent Mixing Zone had the greatest number of actions; these locations had the greatest number of possible detections.

Results and Discussion, con't

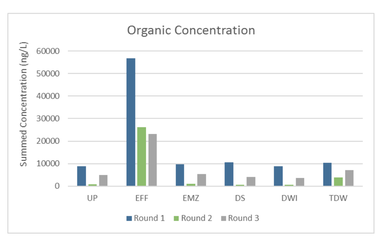
Detection Frequency and Total Quantitative Concentration

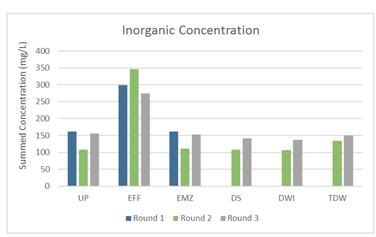




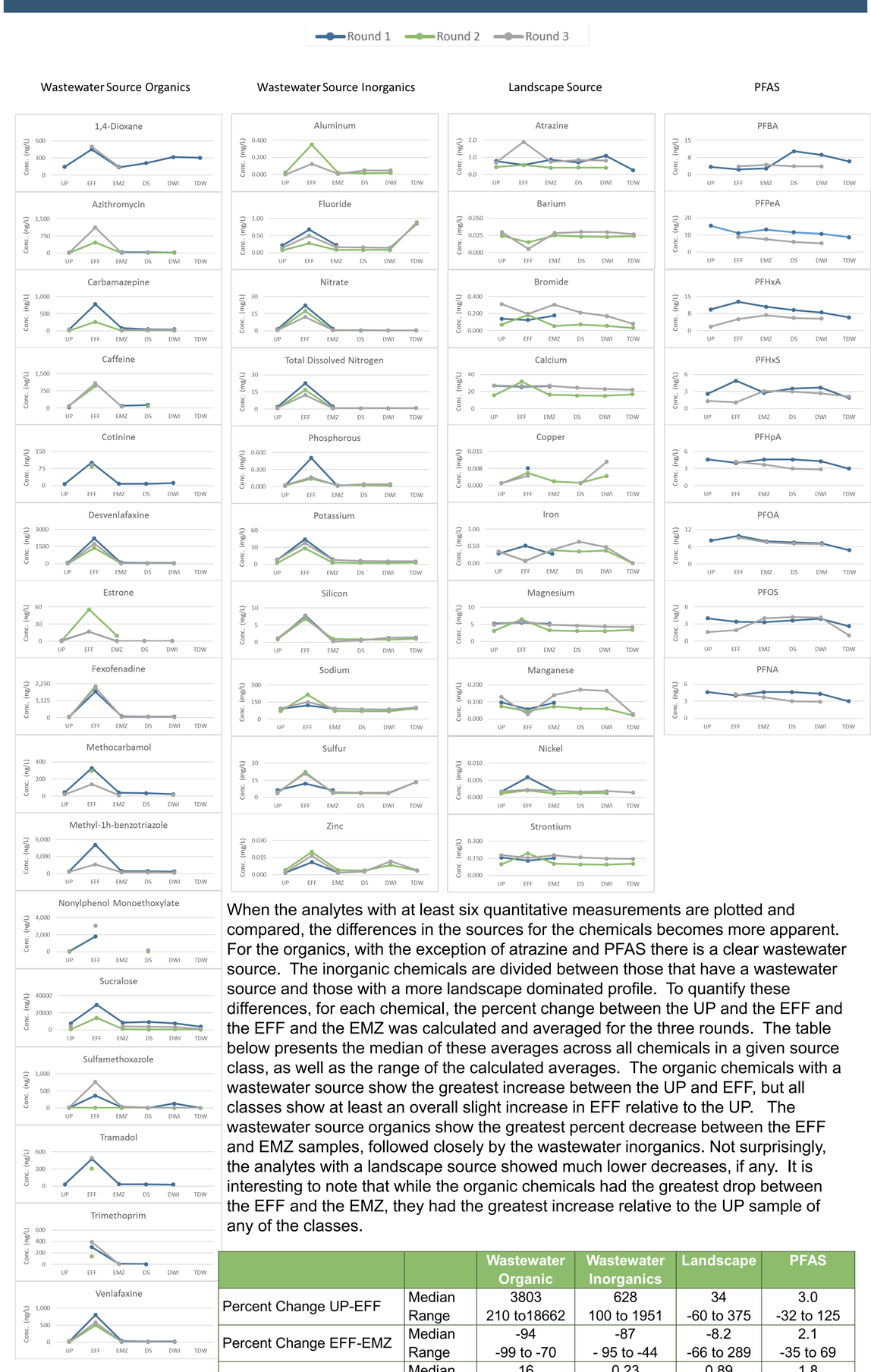


The effluent (EFF) samples had higher frequency of detections when all analytes were considered, and when the organics and inorganics were separated (top row). When the quantitative concentrations were examined (bottom row) the uniqueness of the effluent was even more apparent.





Sources of CECs and Concentration Trends



When the analytes with at least six quantitative measurements are plotted and compared, the differences in the sources for the chemicals becomes more apparent. For the organics, with the exception of atrazine and PFAS there is a clear wastewater source. The inorganic chemicals are divided between those that have a wastewater source and those with a more landscape dominated profile. To quantify these differences, for each chemical, the percent change between the UP and the EFF and the EFF and the EMZ was calculated and averaged for the three rounds. The table below presents the median of these averages across all chemicals in a given source class, as well as the range of the calculated averages. The organic chemicals with a wastewater source show the greatest increase between the UP and EFF, but all classes show at least an overall slight increase in EFF relative to the UP. The wastewater source organics show the greatest percent decrease between the EFF and EMZ samples, followed closely by the wastewater inorganics. Not surprisingly, the analytes with a landscape source showed much lower decreases, if any. It is interesting to note that while the organic chemicals had the greatest drop between the EFF and the EMZ, they had the greatest increase relative to the UP sample of any of the classes.

		Wastewater Organic	Wastewater Inorganics	Landscape	PFAS
Percent Change UP-EFF	Median	3803	628	34	3.0
	Range	210 to18662	100 to 1951	-60 to 375	-32 to 125
Percent Change EFF-EMZ	Median	-94	-87	-8.2	2.1
	Range	-99 to -70	- 95 to -44	-66 to 289	-35 to 69
Percent Change UP-EMZ	Median	16	0.23	0.89	1.8
	Range	-100 to 65	-57 to 12	- 5 to 10	-14 to 145

Conclusions

- *De facto* reuse can result in CECs entering drinking water source waters, and even treated drinking water, but wastewater is not the primary source of all contaminants.
- Organic chemicals with the exception of PFAS and atrazine were clearly associated with a wastewater source.
- A robust quality assurance/ quality control design should be used particularly with concentrations near the reporting limit.

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